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(54) **Metallocene catalysts with Lewis acids and aluminum alkyls**

Metalloccenkatalysator mit Lewisäure und Alkylaluminium

Catalyseurs métallocènes avec acides de Lewis et alkyl-aluminiums

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- JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 110, 1988, pages 1647-1649, American Chemical Society; D. HEDDEN et al.: "[CH₃]₅C₅]2Th(CH₃)₂ surface chemistry and catalysis. direct NMR spectroscopic observation of surface alkylation and ethylene insertion/polymerization on MgCl₂"
- JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 108, 1986, pages 7410-7411, American Chemical Society; R.F. JORDAN et al.: "Ethylene polymerization by a cationic dicyclopentadienylzirconium(IV) alkyl complex"
- MACROMOLECULES, 1989, pages 2186-2189, American Chemical Society; A. ZAMBELLI et al.: "Isotactic polymerization of propene: Homogeneous catalysts based on group 4 metallocenes without methylalumoxane"

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EP 0 427 697 B1

Description

FIELD OF THE INVENTION: This invention relates, in general, to an improved catalyst system and a process for using the improved catalyst system and, specifically, to a catalyst system of a metallocene compound with a Lewis acid and an aluminum alkyl and a process for using the improved catalyst system for polymerization of olefins, primarily propylene.

DESCRIPTION OF RELATED ART: The use of metallocene compounds as catalysts for the polymerization of olefins is known. German patent application No. 2,608,863 discloses a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl)titanium dialkyl, an aluminum trialkyl and water. German patent application No. 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein Y represents $\text{R}_1\text{CH}_2\text{AlR}_2$, $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ where R stands for an alkyl or metallo alkyl, and n is a number within the range 1-4; and the metallocene catalyst is used in combination with an aluminum trialkyl cocatalyst and water.

The use of metallocenes as catalysts in the copolymerization of ethylene and other alpha-olefins is also known in the art. U.S. Pat. No. 4,542,199 to Kaminsky, et al. discloses a process for the polymerization of olefins and particularly for the preparation of polyethylene and copolymers of polyethylene and other alpha-olefins. The disclosed catalyst system includes a catalyst of the formula $(\text{cyclopentadienyl})_2\text{MeRHal}$ in which R is a halogen, a cyclopentadienyl or a $\text{C}_1\text{-C}_6$ alkyl radical, Me is a transition metal, in particular zirconium, and Hal is a halogen, in particular chlorine. The catalyst system also includes an alumoxane having the general formula $\text{Al}_2\text{OR}_4(\text{Al}(\text{R})\text{-O})_n$ for a linear molecule and/or $(\text{Al}(\text{R})\text{-O})_{n+2}$ for a cyclic molecule in which n is a number from 4-20 and R is a methyl or ethyl radical. A similar catalyst system is disclosed in U.S. Pat. No. 4,404,344.

U.S. Pat. No. 4,530,914 discloses a catalyst system for the polymerization of ethylene to polyethylene having a broad molecular weight distribution and especially a bimodal or multimodal molecular weight distribution. The catalyst system is comprised of at least two different metallocenes and an alumoxane. The patent discloses metallocenes that may have a bridge between two cyclopentadienyl rings with the bridge serving to make those rings stereorigid.

European Patent Publication No. 0185918 discloses a stereorigid, chiral zirconium metallocene catalyst for the polymerization of olefins. The application does not indicate that hafnium could be substituted for the zirconium and used to produce a useful polymer product. The bridge between the cyclopentadienyl groups is disclosed as being a linear hydrocarbon with 1-4 carbon atoms or a cyclical hydrocarbon with 3-6 carbon atoms.

Polymerization of olefins is primarily with Ziegler-Natta catalysts. One family of Ziegler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane (MAO) as a cocatalyst. A system for the production of isotactic polypropylene using a titanium or zirconium metallocene catalyst and an alumoxane cocatalyst is described in "Mechanisms of Stereochemical Control in Propylene Polymerization with Soluble Group 4B Metallocene/Methylaluminoxane Catalysts," J. Am. Chem. Soc., Vol. 106, pp. 6355-64, 1984. The article shows that chiral catalysts derived from the racemic enantiomers of ethylene-bridged indenyl derivatives form isotactic polypropylene by the conventional structure predicted by an enantiomeric-site stereochemical control model. The meso achiral form of the ethylene-bridged titanium indenyl diastereomers and achiral zirconocene derivatives, however, produce polypropylene with a purely atactic structure.

MAO activates the metallocene which then becomes able to promote polymerization of alpha-olefins. Other organometallic compounds of aluminum, such as trimethylaluminum (TMA) or dimethyl aluminum halide, are known not to promote polymerization by themselves. Neither aluminum alkyls nor dimethylaluminum halides alone are active cocatalysts.

A combination of TMA and dimethylaluminum fluoride (DMF) has been shown to be effective as a cocatalyst in place of MAO. DMF is a Lewis acid. Such a combination is reported in "Isotactic Polymerization of Propene: Homogeneous Catalysts Based on Group 4 Metallocenes without Methylaluminoxane", A. Zambelli, P. Longo and A. Grassi, Macromolecules, Vol. 22, p. 2186-2189, 1989. The stereochemical structure of the polymers prepared with TMA/DMF and with MAO were very similar. However, the polymerization yields obtained for TMA/DMF mixtures were substantially lower than those obtained for MAO.

It has also been reported that a metallocene compound with magnesium chloride forms a catalyst system with bis(cyclopentadienyl)thorium dimethyl which is effective to polymerize ethylene. Such a combination is reported in "[$(\text{CH}_3)_5\text{C}_5\text{I}_2\text{Th}(\text{CH}_3)_2$ Surface Chemistry and Catalysis. Direct NMR Spectroscopic Observation of Surface Alkylation and Ethylene Insertion/Polymerization on MgCl_2]", D. Heddin and T. J. Marks, J. Am. Chem. Soc., Vol. 110, No.5, 1988. A methyl group is abstracted from the cyclopentadienyl compound and a cation is formed. The methyl group coordinates with the magnesium to form a magnesium anion. Magnesium chloride is a Lewis acid.

Metallocene catalysts are sensitive to poisons in the absence of a scavenging agent, such as methylaluminoxane. Polymerization requires high concentrations of the cations and frequently end up as either runaway reactions or yield no polymer at all.

SUMMARY OF THE INVENTION

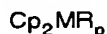
In accordance with the present invention, there is provided a catalyst system of a metallocene compound with a Lewis acid, wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride, and an aluminum alkyl and a process for using the improved catalyst system for polymerization of olefins. Homopolymers or copolymers produced by the polymerization of alpha olefins may be produced in accordance with the present invention. Propagation of the polymer chain is carried out in the presence of a neutral alkyl derivative of a metallocene compound which has been put into contact with a Lewis acid and an aluminum alkyl. Any metallocene catalyst compound having two cyclopentadienyl rings coordinated to a transition metal would be useful in this invention.

The catalyst is contacted with the Lewis acid. The aluminum alkyl is contacted with the olefin. The two mixtures are contacted with each other under polymerization conditions.

DESCRIPTION OF THE INVENTION

This invention is for a catalyst system comprising a metallocene catalyst, a Lewis acid and an aluminum alkyl and a process for using the catalyst system for polymerization of olefins.

The metallocene catalyst is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, halogen, amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4. M is preferably a Group IV metal such as titanium, zirconium or hafnium and is most preferably zirconium. R is preferably an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms. R is most preferably an alkyl or alkoxy up to six carbons atoms or an aryl up to 10 carbon atoms. The neutral derivative of the metallocene is preferably ethylene bis(tetrahydroindenyl)zirconium dimethyl or ethylene bis(indenyl)zirconium dimethyl and is most preferably ethylene bis(indenyl)zirconium dimethyl.

The Lewis acid useful in this invention is any material which can accept an electron pair and is of sufficient acidity to ionize a neutral metallocene to form a cationic metallocene catalyst. In addition, the ligands of the Lewis acid cannot be reactive with the metallocene cation. The Lewis acid of the present invention contains boron or is magnesium chloride (MgCl_2). Preferably, the Lewis acid is tris(pentafluorophenyl)boron.

The aluminum alkyl is of the general formula AlR_3 where R is halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl. Preferably, the aluminum alkyl is trimethyl aluminum (TMA) or triethyl aluminum (TEAL). Most preferably, the aluminum alkyl is triethyl aluminum.

In the practice of this invention, the aluminum alkyl is mixed with the olefin. The Lewis acid is dissolved or slurried in a nonpolar solvent. The neutral metallocene catalyst is dissolved separately in the same solvent. The Lewis acid mixture and the catalyst mixture are combined. The mixture is placed in contact with the blend of olefin and aluminum alkyl. Molar ratios for metallocene:Lewis acid:aluminum alkyl range from 0.01:1:0.1 to 5:1:350 and are preferably from 0.5:1:0.5 to 4:1:25 and are most preferably 0.02:1:1 for Lewis acids which dissolve in a nonpolar solvent and 0.01:1:1 for Lewis acids which form a slurry in nonpolar solvents.

Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80°C to 150°C , preferably 25°C to 90°C and most preferably from 50°C to 80°C .

The following catalyst system were evaluated with and without addition of an aluminum alkyl and with and without addition of a Lewis acid.

1. $\text{iPr}(\text{Cp-1-Flu})\text{ZrMe}_2/\text{F15}/\text{TEAL}$ (TMA)

2. $\text{iPr}(\text{Cp-1-Flu})\text{ZrMe}_2/\text{MgCl}_2/\text{TEAL}$

3. $\text{Et}(\text{Ind})_2\text{ZrMe}_2/\text{F-15}/\text{TEAL}$

4. $\text{Et}(\text{Ind})_2\text{ZrMe}_2/\text{MgCl}_2/\text{TEAL}$

$\text{Et}(\text{Ind})_2\text{ZrMe}_2$ is ethylenebis(indenyl)zirconium dimethyl, $\text{iPr}(\text{Cp-1-Flu})\text{ZrMe}_2$ is isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl and F15 is tris(pentafluorophenyl)boron.

A combination of aluminum alkyl and the above defined Lewis acid was found to be necessary for reproducible, controllable, high efficiency polymerizations.

The invention having been generally described, the following examples are given as particular embodiments of

the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

GROUP 1:

EXAMPLE I

0.16 mmol of triethylaluminum (TEAL) was dissolved in 5 ml of toluene and was added to a 2 liter Zipperclave reactor under 5 psig of nitrogen. Reactor temperature was set to 70° C and one liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

35 mg of $iPr(Cp-I-Flu)ZrMe_2$ was dissolved in 10 ml of toluene. The catalyst was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 70° C and the contents of the reactor were agitated for thirty minutes. At the end of the polymerization, the reactor was cooled and the unreacted propylene was vented from the reactor. There was no reaction product. The results are shown in Table I.

EXAMPLE II

0.33 mmol of triethylaluminum (TEAL) was dissolved in 5 ml of toluene and added to a Zipperclave reactor. Reactor temperature was set to 70° C and 1.0 liter of propylene was added to the reactor. The mixture was stirred for 15 minutes at 1200 rpm.

78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene to form a colorless solution. 60 mg of $iPr(Cp-I-Flu)ZrMe_2$ was dissolved in 10 cc of toluene to form a yellow solution. The two solutions were mixed together and formed a red solution which was mixed for 5 minutes at room temperature.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for thirty minutes. The reactor temperature increased to 90° C. Unreacted propylene was vented from the reactor and the reaction product was washed with acetone and dried in a vacuum.

The polymer was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

EXAMPLE III

The procedure of Example II was repeated using 0.33 mmol of triethyl aluminum (TEAL), 27 mg of tris(pentafluorophenyl)boron and 20 mg of $iPr(Cp-I-Flu)ZrMe_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE IV

The procedure of Example II was repeated using 0.16 mmol of triethyl aluminum (TEAL), 46 mg of tris(pentafluorophenyl)boron and 15 mg of $iPr(Cp-I-Flu)ZrMe_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE V

The procedure of Example II was repeated using 0.10 mmol of triethyl aluminum (TEAL), 46 mg of tris(pentafluorophenyl)boron and 35 mg of $iPr(Cp-I-Flu)ZrMe_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE VI

The procedure of Example II was repeated using 0.16 mmol of triethyl aluminum (TEAL), 46 mg of tris(pentafluorophenyl)boron and 35 mg of $iPr(Cp-I-Flu)ZrMe_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE VII

The procedure of Example II was repeated using 0.33 mmol of triethyl aluminum (TEAl), 46 mg of tris(pentafluorophenyl)boron and 35 mg of $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2$. The contents of the reactor were agitated for thirty minutes. Unreacted propylene was vented from the reactor. There was no reaction product. The results are shown in Table I.

EXAMPLE VIII

The procedure of Example II was repeated using 0.16 mmol of trimethyl aluminum (TMA), 46 mg of tris(pentafluorophenyl)boron and 35 mg of $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

Group 2:

EXAMPLE IX

0.16 mmol of triethyl aluminum (TEAl) was dissolved in 5 ml of toluene and was added to a 2 liter zipperclave reactor under 5 psig of nitrogen.

Reactor temperature was set at 60°C and 1 liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

86 mg of MgCl_2 was slurried in 5 cc of toluene. 18 mg of $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2$ was cannulated into the MgCl_2 slurry. The mixture was stirred for 12 hours to give a dark purple suspension.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for thirty minutes. Unreacted propylene was vented from the reactor and the reaction product was washed with a dilute HCl methanol solution and dried in a vacuum oven.

The polymer was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

Group 3:

EXAMPLE X

One liter of propylene was added to the Zipperclave reactor. Reactor temperature was set to 70 C. 78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene. 58 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ was dissolved in 18 cc of toluene. The two solutions were mixed together for 5 minutes at room temperature.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The reactor temperature was maintained at 70°C and the contents of the reactor were agitated for 35 minutes. Unreacted propylene was vented from reactor. There was no reaction product. The results are shown in Table I.

EXAMPLE XI

0.33 mmol of triethylaluminum (TEA1) was dissolved in 5 ml of non coordinating solvent and added to a Zipperclave reactor. Reactor set point temperature was set to 70° C and 1.0 liter of propylene was added to the reactor. The mixture was stirred for ten minutes at 1200 rpm.

78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene to form a colorless solution. 58 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ was dissolved in 10 cc of toluene to form a pale yellow solution. The two solutions were mixed together to form a clear dark yellow solution which was mixed for 5 minutes at room temperature.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The reactor temperature increased to over 95° C and the contents of the reactor were agitated for six minutes. Unreacted propylene was vented from the reactor and the reaction product was washed with acetone and dried in a vacuum.

The polypropylene reaction product was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

EXAMPLE XII

The procedure of Example XI was repeated using 0.66 mmol of TEAl, 27 mg of tris(pentafluorophenyl)boron and 20 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 22 minutes. The results are shown in Table I.

EXAMPLE XIII

The procedure of Example XI was repeated using 0.33 mmol of TEAl, 2.5 mg of tris(pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

EXAMPLE XIV

The procedure of Example XI was repeated using 0.66 mmol of TEAl, 102 mg of tris(pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

EXAMPLE XV

The procedure of Example XI was repeated using 0.66 mmol of TEAl, 154 mg of tris(pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

EXAMPLE XVI

The procedure of Example XI was repeated using 0.66 mmol of TEAl, 308 mg of tris(pentafluorophenyl)boron and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

Group 4:

EXAMPLE XVII

The procedure of Example IX was repeated with 352 mg of magnesium chloride, 40 mg of Et(Ind)₂ZrMe₂, 0.66 mmol of TEAl and a run time of thirty minutes. The results are shown in Table I.

EXAMPLE XVIII

The procedure of Example IX was repeated with 352 mg of magnesium chloride, 10 mg of Et(Ind)₂ZrMe₂, 0.66 mmol of TEAl and a run time of thirty minutes. The results are shown in Table I.

EXAMPLE XIX

The procedure of Example IX was repeated with 124 mg of magnesium chloride, 40 mg of Et(Ind)₂ZrMe₂, 0.66 mmol of TEAl and a run time of thirty minutes. The results are shown in Table I.

Run #	Catalyst umol (mg)	Lewis Acid umol (mg)	Aluminum Alkyl mmol	Run Time min
1.	iPr(Flu)(Cp)ZrMe ₂ 89.8 (35)	B(C ₆ F ₅) ₃	TEAl 0.16	30

	Run #	Catalyst umol (mg)	Lewis Acid umol (mg)	Aluminum Alkyl mmol	Run Time min
5	2.	153 (60)	153 (78.6)	0.33	30
	3.	51.2 (20)	52.73 (27)	0.33	30
	4.	38.4 (15)	89.8 (46)	0.16	30
10	5.	89.5 (35)	89.8 (46)	0.10	30
	6.	89.5 (35)	89.8 (46)	0.16	30
	7.	89.5 (35)	89.8 (46)	0.33	30
15				TMA	
	8.	89.5 (35)	89.8 (46)	0.16	30
			MgCl ₂	TEAL	
20	9.	45 (18)	900 (86)	0.66	30
	10.	Et (Ind) ZrMe ₂ 154 (58)	B(C ₆ F ₅) ₃ 154 (78.6)	0	35
	11.	154 (58)	154 (78.6)	0.33	6
25	12.	53 (20)	53 (27)	0.66	22
	13.	6.6 (2.5)	6.6 (2.5)	0.33	30
30	14.	6.6 (2.5)	200 (102)	0.66	30
	15.	6.6 (2.5)	300 (154)	0.66	30
	16.	6.6 (2.5)	600 (308)	0.66	30
35		Et (Ind) ZrMe ₂	MgCl ₂	TEAL	
	17.	106 (40)	3700 (352)	0.66	30
	18.	27 (10)	3700 (352)	0.66	30
0	19.	106 (40)	1300 (124)	0.66	30

	Run #	Polymerization Temp °C	Yield	Melting Temp °C	Molecular Weight x 1000	Molecular Weight Distribution
45	1.	70	0	-	-	-
	2.	70	123		57.6	1.9

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	Run #	Polymerization Temp °C	Yield	Melting Temp °C	Molecular Weight x 1000	Molecular Weight Distribution
5	3.	70	7	110	64.3	2.0
	4.	70	58			
	5.	70	5	105	39	2.0
10	6.	70	168	105	61	1.9
	7.	70	110	123	55	2.0
	8.	70	167			
15	9.	60	6	131	57	2.0
	10.	70	0	-	-	-
20	11.	70	117	113	15	4.2
	12.	70	70	122	17.5	3.5
	13.	70	0			
25	14.	70	1	127	26	2.8
	15.	70	90	130	20	5.1
	16.	70	33	129	25	3.7
30	17.	70	49	133	31	1.9
	18.	70	47	130	29	2.4
35	19.	70	8	130	30	2.0

For the F15 catalyst system, higher efficiencies were obtained by increasing the B:Zr molar ratio significantly above 1:1. This implies that the lower efficiencies are partly due to incomplete ionization by F15.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims

1. A catalyst system comprising:

- a) a neutral metallocene compound;
- b) an aluminum alkyl; and
- c) a Lewis acid;

wherein the aluminum alkyl is of the general formula AlR'_3 where R' is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R' being the same or different and at least one R' is an alkyl, wherein the neutral metallocene compound is of the general formula:



wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except when R is a hydride only one R is a hydride and p is from 1 to 4, wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium

chloride, and

wherein the ligands of the Lewis acid are not reactive with the metallocene cation.

2. A catalyst as recited in Claim 1 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
3. A catalyst as recited in Claim 2 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.
4. A catalyst as recited in Claim 1 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
5. A catalyst as recited in Claim 4 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylenebis(indenyl)zirconium dimethyl and isopropylidene(cyclopentadienyl-1-fluorenyl) zirconium dimethyl.
6. A catalyst as recited in Claim 1 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.
7. A catalyst as recited in Claim 6 wherein the aluminum alkyl is triethylaluminum.
8. A catalyst as recited in Claim 1 wherein the Lewis acid is tris(pentafluorophenyl)boron.
9. A process for preparing a catalyst comprising:
 - a) mixing a Lewis acid with a neutral metallocene compound; and
 - b) allowing contact between the Lewis acid and the neutral metallocene compound to form a metallocene compound; and
 - c) adding an aluminum alkyl;
 wherein the neutral metallocene is of the general formula :

$$\text{Cp}_2\text{MR}_p$$
 wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except when R is a hydride only one R is a hydride and p is from 1 to 4;
 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride;
 wherein the ligands of the Lewis acid are not reactive with the metallocene cation; and
 wherein the aluminum alkyl is of the general formula AlR'_3 where R' is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R' being the same or different and at least one R' is an alkyl.
10. A process as recited in Claim 9 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
11. A process as recited in Claim 9 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
12. A process as recited in Claim 11 wherein the M is zirconium.
13. A process as recited in Claim 12 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylenebis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
14. A process as recited in Claim 9 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.
15. A process as recited in Claim 14 wherein the Lewis acid is tris(pentafluorophenyl)boron.
16. A process for polymerization of olefins comprising:

- a) mixing an aluminum alkyl with an olefin;
 b) mixing a neutral metallocene compound with a Lewis acid;
 c) mixing the metallocene-Lewis acid mixture with the aluminum alkyl-olefin mixture.
 wherein the aluminum alkyl is of the general formula AlR'_3 where R' is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R' being the same or different and at least one R' is an alkyl;
 wherein the neutral metallocene compound is of the general formula:



wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except when R is a hydride only one R is a hydride and p is from 1 to 4; and wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.

17. A process as recited in Claim 16 wherein R' is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.
 18. A process as recited in Claim 17 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl ranges from 0.01:1:0.1 to 5:1:350.
 19. A process as recited in claim 18 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl ranges from 0.5:1:0.5 to 4:1:25.
 20. A process as recited in Claim 19 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl is 0.02:1:1.
 21. A process as recited in Claim 19 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl is 0.01:1:1.
 22. A process as recited in Claim 14 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.
 23. A process as recited in Claim 19 wherein the aluminum alkyl is triethylaluminum.
 24. A process as recited in Claim 16 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.
 25. A process as recited in Claim 24 wherein the Lewis acid is tris(pentafluorophenyl)boron.

Patentansprüche

1. Katalysatorsystem, umfassend:

- a) eine neutrale Metallocenverbindung;
 b) ein Aluminiumalkyl; und
 c) eine Lewis Säure;
 worin das Aluminiumalkyl die allgemeine Formel AlR'_3 aufweist, worin R' ein Halogen, Sauerstoff, ein Hydrid, ein Alkyl, ein Alkoxy oder ein Aryl ist, wobei jedes R' gleich oder verschieden ist und mindestens ein R' ein Alkyl ist,
 worin die neutrale Metallocenverbindung die allgemeine Formel:



aufweist, worin Cp ein Cyclopentadienyl oder substituiertes Cyclopentadienyl ist, wobei jedes Cp gleich oder verschieden ist, M ein Metall der Gruppen III, IV, V oder VI ist, R ein Hydrid, ein Halogen, ein Amid oder ein Kohlenwasserstoffrest ist, wobei jedes R gleich oder verschieden ist, außer, daß nur ein R ein Hydrid ist, wenn R ein Hydrid ist, und p von 1 bis 4 beträgt,
 worin die Lewis Säure aus der Gruppe ausgewählt wird, die aus allen Bor und Magnesiumchlorid enthaltenden Lewis Säuren besteht, und worin die Liganden der Lewis Säure nicht mit dem Metallocenkation reagieren können.

2. Katalysator nach Anspruch 1, worin R ein Kohlenwasserstoffrest ist, ausgewählt aus der Gruppe, die aus einem

Alkyl, einem Aryl, einem Alkenyl, einem Alkylaryl und einem Arylalkyl mit bis zu 20 Kohlenstoffatomen besteht.

3. Katalysator nach Anspruch 2, worin R ein Alkyl oder Alkoxy mit bis zu 6 Kohlenstoffatomen oder ein Aryl mit bis zu 10 Kohlenstoffatomen ist.

4. Katalysator nach Anspruch 1, worin das M ein Metall der Gruppe IV ist, ausgewählt aus der Gruppe, die aus Titan, Zirkonium und Hafnium besteht.

5. Katalysator nach Anspruch 4, worin das neutrale Methylderivat eines Metallocens aus der Gruppe ausgewählt wird, die aus Ethylenbis(indenyl)zirkoniumdimethyl und Isopropyliden(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl besteht.

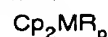
6. Katalysator nach Anspruch 1, worin das Aluminiumalkyl aus der Gruppe ausgewählt wird, die aus Triethylaluminium und Trimethylaluminium besteht.

7. Katalysator nach Anspruch 6, worin das Aluminiumalkyl Triethylaluminium ist.

8. Katalysator nach Anspruch 1, worin die Lewis Säure Tris(pentafluorophenyl)bor ist.

9. Verfahren zur Herstellung eines Katalysators, umfassend:

- a) Mischen einer Lewis Säure mit einer neutralen Metallocenverbindung; und
 - b) Inkontaktbringen der Lewis Säure und der neutralen Metallocenverbindung, wodurch eine Metallocenverbindung gebildet wird; und
 - c) Zugabe eines Aluminiumalkyls,
- worin das neutrale Metallocen die allgemeine Formel:



aufweist, worin Cp ein Cyclopentadienyl oder eine substituierte Cyclopentadienylgruppe ist, wobei jedes Cp gleich oder verschieden ist, M ein Metall der Gruppen III, IV, V oder VI ist, R ein Hydrid, ein Halogen, ein Amid oder ein Kohlenwasserstoffrest ist, wobei jedes R gleich oder verschieden ist, außer, daß nur ein R ein Hydrid ist, wenn R ein Hydrid ist, und p von 1 bis 4 beträgt;

worin die Lewis Säure aus der Gruppe ausgewählt wird, die aus allen Bor und Magnesiumchlorid enthaltenden Lewis Säuren besteht;

worin die Liganden der Lewis Säure nicht mit dem Metallocenkation reagieren können; und

worin das Aluminiumalkyl die allgemeine Formel AlR'_3 aufweist, worin R' ein Halogen, Sauerstoff, ein Hydrid, ein Alkyl, ein Alkoxy oder ein Aryl ist, wobei R' gleich oder verschieden ist und mindestens ein R' ein Alkyl ist.

10. Verfahren nach Anspruch 9, worin R ein Kohlenwasserstoffrest ist, ausgewählt aus der Gruppe, die aus einem Alkyl, einem Aryl, einem Alkenyl, einem Alkylaryl und einem Arylalkyl mit bis zu 20 Kohlenstoffatomen besteht.

11. Verfahren nach Anspruch 9, worin das M ein Metall der Gruppe IV ist, ausgewählt aus der Gruppe, die aus Titan, Zirkonium und Hafnium besteht.

12. Verfahren nach Anspruch 11, worin das M Zirkonium ist.

13. Verfahren nach Anspruch 12, worin das neutrale Derivat eines Metallocens aus der Gruppe ausgewählt wird, die aus Ethylenbis(indenyl)zirkoniumdimethyl und Isopropyliden(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl besteht.

14. Verfahren nach Anspruch 9, worin die Lewis Säure aus der Gruppe ausgewählt wird, die aus allen Bor und Magnesiumchlorid enthaltenden Lewis Säuren besteht.

15. Verfahren nach Anspruch 14, worin die Lewis Säure Tris(pentafluorophenyl)bor ist.

16. Verfahren zur Polymerisation eines Olefins, umfassend:

- a) Mischen eines Aluminiumalkyls mit einem Olefin;

b) Mischen einer neutralen Metallocenverbindung mit einer Lewis Säure;
 c) Mischen der Metallocen-Lewis-Säure-Mischung mit der Aluminiumalkyl-Olefin-Mischung,
 worin das Aluminiumalkyl die allgemeine Formel AlR'_3 aufweist,
 worin R' ein Halogen, Sauerstoff, ein Hydrid, ein Alkyl, ein Alkoxy oder ein Aryl ist, wobei jedes R' gleich oder
 verschieden ist und mindestens ein R' ein Alkyl ist;
 worin die neutrale Metallocenverbindung die allgemeine Formel:



aufweist, worin Cp Cyclopentadienyl oder substituiertes Cyclopentadienyl ist, wobei jedes Cp gleich oder ver-
 schieden ist, M ein Metall der Gruppen III, IV, V oder VI ist, R ein Hydrid, ein Halogen, ein Amid oder ein
 Kohlenwasserstoffrest ist, wobei jedes R gleich oder verschieden ist, außer, daß nur ein R ein Hydrid ist, wenn
 R ein Hydrid ist, und p von 1 bis 4 beträgt; und worin die Lewis Säure aus der Gruppe ausgewählt wird, die
 aus allen Bor und Magnesiumchlorid enthaltenden Lewis Säuren ausgewählt wird.

17. Verfahren nach Anspruch 16, worin R' ein Alkyl oder Alkoxy mit bis zu 6 Kohlenstoffatomen oder ein Aryl mit bis
 zu 10 Kohlenstoffatomen ist.

18. Verfahren nach Anspruch 17, worin das molare Verhältnis von Metallocen:Lewis Säure:Aluminiumalkyl im Bereich
 von 0,01:1:0,1 bis 5:1:350 liegt.

19. Verfahren nach Anspruch 18, worin das molare Verhältnis von Metallocen:Lewis Säure:Aluminiumalkyl im Bereich
 von 0,5:1:0,5 bis 4:1:25 liegt.

20. Verfahren nach Anspruch 19, worin das molare Verhältnis von Metallocen:Lewis Säure:Aluminiumalkyl 0,02:1:1
 beträgt.

21. Verfahren nach Anspruch 19, worin das molare Verhältnis von Metallocen:Lewis Säure:Aluminiumalkyl 0,01:1:1
 beträgt.

22. Verfahren nach Anspruch 14, worin das Aluminiumalkyl aus der Gruppe ausgewählt wird, die aus Triethylaluminium
 und Trimethylaluminium besteht.

23. Verfahren nach Anspruch 19, worin das Aluminiumalkyl Triethylaluminium ist.

24. Verfahren nach Anspruch 16, worin die Lewis Säure aus der Gruppe ausgewählt wird, die aus allen Bor und Magne-
 siumchlorid enthaltenden Lewis Säuren besteht.

25. Verfahren nach Anspruch 24, worin die Lewis Säure Tris(pentafluorophenyl)bor ist.

Revendications

1. Système catalytique comprenant :

- a) un composé métallocène neutre;
- b) un alkyl-aluminium; et
- c) un acide de Lewis;

dans lequel l'alkyl-aluminium a la formule générale AlR'_3 où R' est un halogène, un oxygène, un hydruure, un
 alkyle, un alkoxy ou un aryl, chaque R' étant identique ou différent, et au moins un R' étant un alkyle,

dans lequel le composé métallocène neutre a la formule générale :



où Cp est un cyclopentadiényle ou un cyclopentadiényle substitué, chaque Cp étant identique ou différent, M
 est un métal du groupe III, IV, V ou VI, R est un hydruure, un halogène, une amine ou un radical hydrocarboné,
 chaque R étant identique ou différent, sauf si R est un hydruure auquel cas un R seulement est un hydruure, et
 p vaut de 1 à 4,

dans lequel l'acide de Lewis est choisi parmi le groupe constitué de tous les acides de Lewis contenant du bore et le chlorure de magnésium, et

dans lequel les ligands de l'acide de Lewis ne sont pas réactifs avec le cation métallocène.

2. Catalyseur selon la revendication 1 dans lequel R est un radical hydrocarboné choisi parmi le groupe constitué des alkyle, aryl, alkényle, alkylaryl ou arylalkyl ayant jusqu'à 20 atomes de carbone.

3. Catalyseur selon la revendication 2 dans lequel R est un alkyle ou un alkoxy ayant jusqu'à six atomes de carbone ou un aryl ayant jusqu'à 10 atomes de carbone.

4. Catalyseur selon la revendication 1 dans lequel M est un métal du groupe IV choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium.

5. Catalyseur selon la revendication 4 dans lequel le dérivé de méthyl neutre du métallocène est choisi parmi le groupe constitué de l'éthylènebis(indényle)zirconium diméthyle et de l'isopropylidène(cyclopentadiényle-1-fluorényle) zirconium diméthyle.

6. Catalyseur selon la revendication 1 dans lequel l'alkyl-aluminium est choisi parmi le groupe constitué du triéthyl-aluminium et du triméthyle-aluminium.

7. Catalyseur selon la revendication 6 dans lequel l'alkyl-aluminium est le triéthyl-aluminium.

8. Catalyseur selon la revendication 1 dans lequel l'acide de Lewis est le tris(pentafluorophényle) de bore.

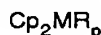
9. Procédé de préparation d'un catalyseur comprenant :

a) mélanger un acide de Lewis avec un composé de métallocène neutre; et

b) permettre le contact entre l'acide de Lewis et le composé de métallocène neutre pour former un composé métallocène; et

c) ajouter un alkyl-aluminium;

dans lequel le métallocène neutre a la formule générale :



où Cp est un groupe cyclopentadiényle ou cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe III, IV, V ou VI, R est un hydruure, un halogène, une amine ou un radical hydrocarboné, chaque R étant identique ou différent, sauf si R est un hydruure auquel cas seulement un R est un hydruure, et p vaut de 1 à 4;

dans lequel l'acide de Lewis est choisi parmi le groupe constitué de tous les acides de Lewis contenant du bore et le chlorure de magnésium;

dans lequel les ligands de l'acide de Lewis ne sont pas réactifs avec le cation métallocène; et

dans lequel l'alkyl-aluminium a la formule générale AlR'_3 où R' est un halogène, un oxygène, un hydruure, un alkyle, un alkoxy ou un aryl, chaque R' étant identique ou différent, et au moins un R' étant un alkyle.

10. Procédé selon la revendication 9 dans lequel R est un radical hydrocarboné choisi parmi le groupe constitué des alkyle, aryl, alkényle, alkylaryl ou arylalkyl ayant jusqu'à 20 atomes de carbone.

11. Procédé selon la revendication 9 dans lequel M est un métal du groupe IV choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium.

12. Procédé selon la revendication 11 dans lequel M est le zirconium.

13. Procédé selon la revendication 12 dans lequel le dérivé neutre du métallocène est choisi parmi le groupe constitué

de l'éthylènebis(indényle)zirconium diméthyle et de l'isopropylidène(cyclopentadiényle-1-fluorényl)zirconium diméthyle.

14. Procédé selon la revendication 9 dans lequel l'acide de Lewis est choisi parmi le groupe constitué de tous les acides de Lewis contenant du bore et le chlorure de magnésium.

15. Procédé selon la revendication 14 dans lequel l'acide de Lewis est le tris(pentafluorophényle) de bore.

16. Procédé pour la polymérisation d'oléfines comprenant :

- a) mélanger un alkyl-aluminium avec une oléfine;
- b) mélanger un composé métallocène neutre avec un acide de Lewis;
- c) mélanger le mélange métallocène-acide de Lewis avec le mélange alkyle-aluminium-oléfine;

dans lequel l'alkyl-aluminium a la formule générale AlR'_3 où R' est un halogène, un oxygène, un hydruure, un alkyle, un alkoxy ou un aryle, chaque R' étant identique ou différent, et au moins un R' étant un alkyle;

dans lequel le composé métallocène neutre a la formule générale :



où Cp est un cyclopentadiényle ou un cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe III, IV, V ou VI, R est un hydruure, un halogène, une amine ou un radical hydrocarboné, chaque R étant identique ou différent, sauf si R est un hydruure auquel cas un R seulement est un hydruure, et p vaut de 1 à 4; et

dans lequel l'acide de Lewis est choisi parmi le groupe constitué de tous les acides de Lewis contenant du bore et le chlorure de magnésium.

17. Procédé selon la revendication 16 dans lequel R' est un alkyle ou un alkoxy ayant jusqu'à six atomes de carbone ou un aryle ayant jusqu'à 10 atomes de carbone.

18. Procédé selon la revendication 17 dans lequel le rapport molaire métallocène:acide de Lewis:alkyl-aluminium va de 0,01:1:0,1 à 5:1:350.

19. Procédé selon la revendication 18 dans lequel le rapport molaire métallocène:acide de Lewis:alkyl-aluminium va de 0,5:1:0,5 à 4:1:25.

20. Procédé selon la revendication 19 dans lequel le rapport molaire métallocène:acide de Lewis:alkyl-aluminium est de 0,02:1:1.

21. Procédé selon la revendication 19 dans lequel le rapport molaire métallocène:acide de Lewis:alkyl-aluminium est de 0,01:1:1.

22. Procédé selon la revendication 14 dans lequel l'alkyl-aluminium est choisi parmi le groupe constitué du triéthyl-aluminium et du triméthyle-aluminium.

23. Procédé selon la revendication 19 dans lequel l'alkyl-aluminium est le triéthyl-aluminium.

24. Procédé selon la revendication 16 dans lequel l'acide de Lewis est choisi parmi le groupe constitué de tous les acides de Lewis contenant du bore et le chlorure de magnésium.

25. Procédé selon la revendication 24 dans lequel l'acide de Lewis est le tris(pentafluorophényle) de bore.